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Preliminary communication

Phenylation of cationic allylpalladium(II) complexes by tetraphenylborate anion. A mechanistic study

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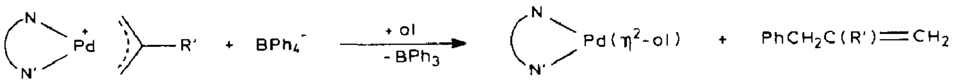
Abstract

The mechanism of the reaction of allyl complexes $[Pd(\eta^3\text{-}2\text{-}R'C_3H_4)(N{-}N')]^+$ ($N{-}N' = \alpha$-diimine ligand) wiht BPh_4^- in the presence of activated olefins (ol), yielding the products $[Pd(\eta^2\text{-ol})(N{-}N')]$ and $PhCH_2C(R'){=}CH_2$, has been investigated. The results are interpreted in terms of extensive association between the cationic substrate and the BPh_4^- anion in a tight ion-pair, followed by rate-determining phenyl transfer to the palladium center and fast reductive elimination of allylbenzene.

In recent years the chemistry of η^3-allylpalladium complexes as intermediates in organic syntheses has received considerable attention [1]. Among the reactions studied, of prime importance is carbon–carbon bond formation by reductive elimination [2]. In particular, the mechanism of reductive coupling between the coordinated allyl moiety and aryl groups has been investigated very recently [3]. During a study of the solution behaviour of the pyridine-2-carbaldimine complexes $[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)(py\text{-}2\text{-}CH{=}NR)]X$ we noted that the complex with $R = C_6H_4OMe\text{-}4$ and $X = BPh_4^-$ underwent rapid decomposition to $PhCH_2C(Me){=}CH_2$ and palladium metal at ambient temperature [4]. We have now carried out a mechanistic investigation of this reaction in the presence of an activated olefin (eq. 1).



(1) (2) (3)

(1)

$[N{-}N' = 2,2'$-bipyridine, py-2-CH=NR ($R = C_6H_4OMe\text{-}4$,Me,CMe_3),RN=CH–CH=NR ($R = C_6H_4OMe\text{-}4$); $R' =$ H,Me; ol = dimethylfumarate (dmf), fumaronitrile (fn)]

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Table 1

Pseudo-first order rate constants for reaction 1 (ol = dmf) [a]

N–N′	R′	k_{obs} (s^{-1})
py-2-CH=NR		
R = CMe_3	H	$7.5(\pm 0.8) \times 10^{-4}$
R = Me	H	$6.0(\pm 1.0) \times 10^{-4}$
R = C_6H_4OMe-4	H	$2.98(\pm 0.07) \times 10^{-3}$
R = C_6H_4OMe-4	Me	$1.8(\pm 0.2) \times 10^{-3}$
RN=CH–CH=NR		
R = C_6H_4OMe-4	Me	[b]
R = CMe_3	Me	[b]

[a] At 25 °C in aqueous (2% v/v) methanol. [b] Too fast to measure.

The allylbenzenes **3** are formed in almost quantitative yields (> 95%), as indicated by ^1H NMR spectroscopy and GLC-MS experiments. The palladium(0)-olefin derivatives **2** were isolated in good yields (70–80%) and fully characterized [5*].

The reaction mechanism does not appear to involve a single-electron transfer between the ionic species since addition of an efficient radical scavenger, such as 1,4-cyclohexadiene [6], does not appreciably affect the reaction rate. On the other hand, the rates are found to depend on the α-diimine ligand in the following sequences: 2,2′-bipyridine < py-2-CH=NR < RN=CH–CH=NR (R = C_6H_4OMe-4), py-2-CH=$NCMe_3$ = py-2-CH=NME < py-2-CH=NC_6H_4OMe-4 and RN=CMe–CMe=NR < RN=CH-CH=NR (R = C_6H_4OMe-4). Both steric and electronic properties of the α-diimine are important. In particular, the rates increase with increasing π-accepting ability of the N–N′ ligand [7], and with decreasing steric requirements of the imino-carbon substituents. The reactivity is slightly decreased when the R′-allyl substituent is changed from H to Me, whereas it is hardly affected by the nature of the olefin. A marked solvent effect is also observed, with the rates falling in the order: dichloromethane > 1,2-dichloroethane > acetone ≫ acetonitrile. A kinetic study of reaction 1 under pseudo-first order conditions in aqueous (2% v/v) methanol, reveals that the kinetics obey eq. 2, where the significance of *k* is shown in Scheme 1.

$$k_{obs} = k_1 \qquad (2)$$

The rates are independent of both the BPh_4^- and olefin concentrations (Table 1), and also of the ionic strength in the range $0-3 \times 10^{-3}$ mol dm^{-3} ($LiClO_4$). On the basis of conductivity measurements, ^1H NMR data, and GLC-MS experiments [8 *], we propose the mechanism shown in Scheme 1, which involves rapid and virtually quantitative association between the cationic species **1** and the BPh_4^- anion, followed by slow, rate-determining phenyl tranfer to yield a labile intermediate II, with both phenyl and allyl groups bound to the metal, which undergoes rapid reductive elimination of allylbenzene. The ensuing palladium(0) fragment is immediately stabilized by coordination of the activated olefin.

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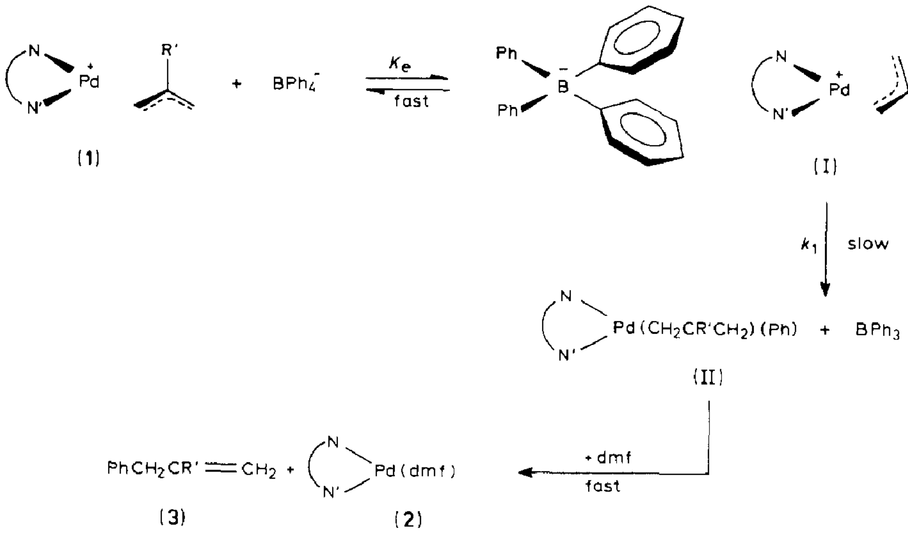
* Reference number with asterisk indicates a note in the list of references.



The kinetic equation has the general form as shown in eq. 3 and this reduces to equation 2 when $K_e[\mathrm{BPh_4}^-] \gg 1$.

$$k_{obs} = \frac{k_1 K_e [\mathrm{BPh_4}^-]}{1 + K_e [\mathrm{BPh_4}^-]} \tag{3}$$

The large extent of ion-pairing between the cationic substrate **1** and $\mathrm{BPh_4}^-$ is confirmed by the high values of the association equilibrium constants K_e, determined by the Shedlovsky treatment of molar conductivity vs. concentration data [9] in absolute methanol at 25 °C for the complexes $[\mathrm{Pd}(\eta^3\text{-}2\text{-}\mathrm{MeC_3H_4})(\mathrm{TMEDA})]\mathrm{BPh_4}$ ($K_e = 2950 \pm 80$; TMEDA = tetramethylethylenediamine) and $[\mathrm{Pt}(\eta^3\text{-}2\text{-}\mathrm{MeC_3H_4})(\text{py-2-CH=NR})]\mathrm{BPh_4}$ ($K_e = 14500 \pm 400$; $\mathrm{R} = \mathrm{C_6H_4OMe}$-4), which do not undergo the phenyl transfer reaction 1. The specific interaction of tetraphenylborate anion with the cationic complexes **1** is particularly evident in the ^{1}H NMR spectra of $[\mathrm{Pd}(\eta^3\text{-}2\text{-}\mathrm{MeC_3H_4})(\text{py-2-CH=NC}_6\mathrm{H_4OMe}\text{-4})]\mathrm{X}$ ($\mathrm{X}^- = \mathrm{ClO_4}^-$, $\mathrm{BPh_4}^-$). In $\mathrm{CD_2Cl_2}$, the N=C–H imino proton and the H(3) and H(6) 2-pyridyl proton resonances at 8.78, 8.22, and 8.83 ppm, respectively, for $\mathrm{X}^- = \mathrm{ClO_4}^-$, are shifted upfield to 7.87, ~ 7.6, and 8.43 ppm, respectively, for $\mathrm{X}^- = \mathrm{BPh_4}^-$, owing to the shielding effect of phenyl ring currents of $\mathrm{BPh_4}^-$ anion in a tight ion-pair of type I [4]. In $\mathrm{CD_3CN}$ and $(\mathrm{CD_3})_2\mathrm{CO}$, however, such a shielding disappears and the N=C–H, H(3), and H(6) chemical shifts for $\mathrm{X}^- = \mathrm{BPh_4}^-$ are comparable with those of the corresponding perchlorate derivative in the same solvents. This behaviour can be rationalized in terms of a fast equilibrium association between the cationic complex and the $\mathrm{BPh_4}^-$ anion, which is shifted well over towards the ion-pair I in $\mathrm{CD_2Cl_2}$, whereas in $\mathrm{CD_3CN}$ and $(\mathrm{CD_3})_2\mathrm{CO}$ the ionic species are predominant. The solvent dependence of the association equilibrium reflects the observed sequence of reactivities, and can be interpreted in terms of a balance of the solvating abilities (as indicated by the dielectric constant) and coordinating abilities of the solvents. Thus, in acetonitrile, which has both a high dielectric constant and a high coordinating ability, the reaction is so slow that kinetic studies cannot be carried out.

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References and notes

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